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# Enhancing polyethersulfone/dragon blood resin – iron membrane chemical stability with coordinated covalent compounds

Aulia Chintia Ambarita<sup>1,2</sup>, Sri Mulyati<sup>2,\*</sup>, Nasrul Arahman<sup>2</sup>, Muhammad Roil Bilad<sup>3</sup>, Rinal Diaul Haikal<sup>4</sup>, Bahar Yavuztürk Gül<sup>5</sup>, Sevde Korkut<sup>5</sup>, İsmail Koyuncu<sup>5</sup>

- <sup>1</sup> Doctoral Program, School of Engineering Science, Syiah Kuala University, Jalan Syeh Abdur Rauf, Banda Aceh 23111, Indonesia
- <sup>2</sup> Department of Chemical Engineering, Syiah Kuala University, Jalan Syeh Abdur Rauf, Banda Aceh 23111
- <sup>3</sup> Faculty of Integrated Technologies, Universiti Brunei Darussalam, Jalan Tungku Link, Bandar Seri Begawan BE1410, Brunei\_
- <sup>4</sup> Magister of Chemical Engineering, Engineering Faculty, Syiah Kuala University, Jalan Syeh Abdur Rauf, Banda Aceh 23111, Indonesia
- <sup>5</sup> National Research Center on Membrane Technologies, Istanbul Technical University, Maslak 34469, Istanbul, Turkey
- \* Corresponding author's e-mail: sri.mulyati@usk.ac.id

# ABSTRACT

PES/DBR membranes are known to exhibit instability when exposed to strong alkaline conditions, primarily due to the leaching of additives and the degradation of polyphenolic compounds. The study explores the effect of  $Fe^{3+}$  concentration on the properties and performance of PES/DBR-Fe membranes. Five types of membranes were prepared with varying concentrations of  $Fe^{3+}$  from 0 - 0.05 M in the coagulation bath. Membranes were subjected to evaluation considering their characteristics, performance, and chemical stability under strong alkaline solution (NaOH 0.01 N for 48 h). The results indicate that increasing the  $Fe^{3+}$  concentration had minimal effects on contact angle, water uptake, and membrane functional groups. However, it notably influenced the cross-sectional structure and porosity of the membrane. Higher  $Fe^{3+}$  concentrations led to a decrease in pure permeability but maintained a satisfactory rejection rate of >95%. Of all the concentrations investigated, the membrane with a 0.05 M exhibits the smallest increase in flux ratio, thus demonstrating the highest stability. This study explores strategies to enhance the chemical stability of membrane, focusing on the incorporation of novel coordinated covalent compounds between anthocyanin and  $Fe^{3+}$ .

**Keyword:** dragon blood resin, chemical stability, coordinated covalent compounds, polyethersulfone, antifouling properties.

# INTRODUCTION

In recent decades, membrane technology has experienced significant advancement. Membrane separation technology has gained widespread recognition and is frequently employed to address a variety of industrial and environmental challenges (Sahu et al., 2024). Among the diverse array of polymers used for membrane production, polyethersulfone (PES) stands out due to its commendable attributes, such as high thermal stability, resistance to pressure, hydrolytic stability, exceptional oxidative resistance, and durability in the presence of organic solvents (Seah et al., 2024). However, the hydrophobic nature of PES membranes renders them susceptible to fouling, a common issue resulting from the accumulation of impurities that obstruct the membrane pores, consequently reducing the flux (Molina et al., 2024).

Traditionally, PES polymers have been combined with various inorganic additives, substantially enhancing mechanical stability and permeability (Abubakar et al., 2024; Mataram et al., 2024). Fouling remains a significant challenge with membranes, necessitating the hydrophilic modification of inherently hydrophobic PES membranes. Various techniques have been proposed to combat fouling, including coating (Desiriani et al., 2024), blending with hydrophilic and amphiphilic polymers (Wang et al., 2024), grafting with hydrophilic monomers, grafting with short-chain molecules, and surface functionalization. While fouling can be mitigated through backwashing, this process incurs high costs and may curtail the membrane's service life.

A recent trend involves incorporating biomaterials into PES membranes to augment their antifouling properties. These biomaterials encompass inorganic compounds derived from biomass, extracts, and plant-based resins (Ambarita, Mulyati, Arahman, & Bilad, 2024). Notably, Dragon Blood resin (DBR), a natural resin, has been reported to enhance PES membrane performance. The PES/DBR membrane has demonstrated promising attributes, maintaining effective antifouling properties and significantly increasing pure water flow rates (Ambarita et al., 2021). Nevertheless, bio-additives like DBR have limitations due to less stable chemical bonds, leading to DBR leaching during membrane washing and subsequent pore size enlargement (Ambarita, Mulyati, Arahman, Bilad, et al., 2024).

Several strategies can be employed to increase membrane stability. One of the most effective strategies is through the formation of coordinate covalent bonds. This modification has been widely reported in literature using tannin acid additives (Jiang et al., 2021; Wu et al., 2019). In this approach, Fe<sup>3+</sup> was the co-components most often used to impose the compatibility of tannin acid in polymer matric. The three galloyl groups of tannic acid can react with each Fe<sup>3+</sup> to form a stable octahedral complex (Yang et al., 2015). The galloyl group is a polyphenol unit with many hydroxyl groups (-OH) and carboxyl groups (-COOH), which can act as electron donors. This group can coordinate with the Fe<sup>3+</sup> by donating a lone pair of electrons.  $Fe^{3+}$  is a metal ion that can accept electron pairs from the galloyl group. It can form coordinate covalent bonds with the oxygen atom of the hydroxyl group in the galloyl group (Chen et al., 2024).

This study explored coordinate covalent bonds to enhance the compatibility of additive into the polymer matric by formation of coordinate covalent bonds between DBR and  $Fe^{3+}$ . This research investigated the effect of  $Fe^{3+}$  concentration on the characteristics and performance of PES/DBR-Fe membranes, specifically on the chemical stability of the

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specifically on the chemical stability of the membrane evaluated by monitoring the change of the permeation rate ratio and the change in the humic acid rejection ratio after the membrane samples were exposed to a strong base (pH: 12). It was hypothesized that membrane stability could be achieved by formation of coordinated covalent bond between DBR resided in the membrane matric when exposed to Fe<sup>3+</sup>.

Five PES/DBR membrane samples were prepared using the immersion precipitation phase inversion method. The formation of Fe<sup>3+</sup> was introduced in the membrane by dissolving it at various concentrations in water used as nonsolvent in the coagulation bath. After fabrication and characterization, the stability of the membrane samples was evaluated by exposure to alkali solution for 48 hours. The pure water permeability, humic acid permeability, and rejection were measured before and after immersion to evaluate the stability of the membranes.

# EXPERIMENTAL

# Materials

PES (Ultrason E 6020 P, MW 58.000 Da, BASF) and 1-N-methyl-2-pyrrolidone (NMP 99.5%, Merck) were used as the polymer and the solvent for preparing the dope solution, while DBR as additive. The DBR was purchased from local farmer in Aceh Besar, Indonesia. Iron (III) chloride hexahydrate (FeCl<sub>3</sub>.6H<sub>2</sub>O, Merck), humic acid (technical grade 50–60%, Sigma Aldrich), and sodium hydroxide (NaOH, Sigma Aldrich) were used for formation of complex coordination covalent compound, organic foulant, and alkaline agent, respectively.

# Preparation of PES/DBR-Fe membrane

The immersion precipitation phase inversion method was employed to prepare five flat sheets of membrane. A 3%(w/w) DBR was firstly dissolved in 82.5% (w/w) NMP for 20 minutes. Then, 14.5%(w/w) PES was added slowly while stirring for 24 hours. The dope solution was subsequently allowed to rest for 4 hours to eliminate entrapped air bubbles. The dope solution was then cast on a glass plate with a wet casting thickness of 250 µm, followed by immersion in the coagulation bath containing water as the non-solvent for 2-4 minutes. The concentration of Fe<sup>3+</sup> in the dope solution was varied as the independent variable at concentration of 0, 0.001, 0.005, 0.01 and 0.05 M. The illustration of PES/DBR-Fe membrane preparation is shown in Figure 1. The 3% DBR concentration in the dope solution was chosen based on our prior research which showed the most optimum performance. It was reported that the incorporation of 3% DBR had a positive impact on the characteristics and performance of the resulting PES membranes. However, as the flux recovery ratio (FRR) was greater than 100%, additive release occurred during the filtration which was addressed by increasing the membrane stability in the present work (Ambarita et al., 2021).

#### Characterization of PES/DBR-Fe membrane

To determine the hydrophilicity of the membrane, the static water contact angle method was employed (KSV Attension Theta model). The measurement involved attaching the sample to a glass surface using tape, then dropping a 7 µL of distilled water to the membrane surface. Multiple measurements were taken for each membrane. An ATR-FTIR (PerkinElmer spectrum 100 FT-IR), was used to identify the functional groups present on the membrane surface, and the resulting spectra were analysed through principal statistically component analysis (PCA). The scanning electron microscopy (SEM) device (FEI Quanta-250) was used to visualize the cross-sectional structure of each membrane, while the SEM-EDX device (Phenom ProX, Thermo scientific, Japan) was used to analyse the elemental compositions on the membrane surface and cross-sectional. In addition, the membrane's porosity and water uptake were determined using the gravimetric

method to compare results. The Guerout-Elford-Ferry equation was used to determine the pore size, following the same procedure in an earlier work (Ambarita et al., 2021).

#### **Evaluation of PES/DBR-Fe performances**

There were three key performance parameters evaluated for each membrane, namely permeability, rejection, and flux recovery. A crossflow filtration module with a membrane surface area of 9.075 cm<sup>2</sup> was used and operated at a constant transmembrane pressure of 1 bar. The permeability was measured by filtering distilled water and 50 mg/L humic acid solution in the following order: 1.5 hours of compaction and 1 hour of data collection. The data collection was done in 10-minute intervals. The concentration of humic acid in the permeate was analysed using a UV-Vis spectrometer. The pure water permeability  $(J_{u}, L/m^2 \cdot h \cdot bar)$  and humic acid permeability  $(J_{ha}, L/m^2 \cdot h \cdot bar)$  were calculated using Equation 1, while the humic acid rejection (R, %) was evaluated using Equation 2. The flux recovery (FRR, %) was obtained using Equation 3.

$$J = \frac{V}{A t \Delta P} \tag{1}$$

$$R = 1 - \frac{c_p}{c_f} \tag{2}$$

$$FRR(\%) = 1 - \frac{J_{W2}}{J_{W1}}$$
(3)

where: V is volume of permeate (L) at the time t (h), A is effective membrane area (m<sup>2</sup>),  $\Delta P$ is a transmembrane pressure (bar),  $C_p$  and  $C_f$  are permeate and feed of humic acid concentration (mg/L), respectively.

#### **Chemical stability**

Each membrane was immersed in a 50 mL solution of 0.01N NaOH (pH: 12) for 48 hours.



Figure 1. Preparation of PES/DBR-Fe membrane

The values of pure water permeability, humic acid permeability, and rejection before and after immersion were compared to evaluate the membrane stability.

# **RESULT AND DISCUSSION**

# Effect of Fe<sup>3+</sup> concentration on membrane characteristics

# Surface hydrophilicity

The effect of Fe<sup>3+</sup> concentration on membrane surface hydrophilicity is summarized in Table 1. The chemical composition and functional groups present on the surface of the membrane can affect its wettability. Hydrophilic groups such as hydroxyl (-OH) or carboxyl (-COOH) groups increase the surface energy of the membrane and make it more wettable. Table 2 shows that the concentration of Fe<sup>3+</sup> had insignificant effect on the surface hydrophilicity of the membrane, with an average of 3.94%. The highest contact angle was achieved in M-3 with of Fe<sup>3+</sup> of 0.05 M, while the lowest was at a  $Fe^{3+}$  of 0 M, with only a difference of  $\pm 3^{\circ}$ . The trend shown by the contact angle test was fluctuating. Membranes with Fe<sup>3+</sup> of 0.001 and 0.005 M showed higher hydrophilicity, while at 10× higher concentration, the membranes were more hydrophobic.

The findings on water contact angle were supported by the water uptake test results, where generally membranes with lower contact angles had higher wetting properties. An increase in the concentration of Fe<sup>3+</sup> did not significantly affect the water uptake, with an average of 1.44%. The highest was obtained in membrane M-3 with a concentration of Fe<sup>3+</sup> of 0.005 M, while the lowest was at a Fe<sup>3+</sup> of 0.05 M, with only differences of  $\pm 2.89\%$ .

In general, a higher Fe<sup>3+</sup> concentration in the coagulation bath led to a more hydrophilic membrane surface. This is because Fe<sup>3+</sup> ions can react with functional groups on the membrane surface, forming metal complexes that increase the surface charge and promote water adsorption. Additionally, Fe<sup>3+</sup> ions can promote the formation of a more open, porous membrane structure that can enhance water permeability. The trend peak at certain concentration from which the opposite effects were observed.

# FTIR spectra

The results of the FTIR analysis in Figure 2 show the same peak in all membranes, and no new characteristic peak was found in the main chain of PES. In the fingerprint region (650–1300 cm<sup>-1</sup>), C-H groups were indicated at peak numbers of 871, 835, 717, 717, and 700 cm<sup>-1</sup> from the alkene

Table 1. The effect of Fe<sup>3+</sup> concentration on contact angle and water uptake

	0 1	
Conc. Fe <sup>3+</sup> (M)	Water contact angle (°)	Water uptake (%)
0	58.66 ± 2.37	73.37 ± 1.73
0.001	60.20 ± 2.40	74.65 ± 1.29
0.005	59.07 ± 3.05	75.59 ± 2.37
0.01	61.96 ± 1.49	73.43 ± 2.49
0.05	62.66 ± 3.27	72.70 ± 0.99

**Table 2.** Effect of  $Fe^{3+}$  co-component concentration on SEM-EDX elemental composition on the surface and cross section of the membrane.

Conc. of Fe³⁺ in coagulation bath (M)	Atomic percentage (At %)					
	С	0	N	S	Fe	
Surface						
0	74.67	12.02	6.81	6.26	0.020	
0'01	69.94	17.26	6.74	5.58	0.250	
0.05	70.72	14.58	1.27	1.67	10.550	
Cross-section						
0	56.38	18.32	18.54	6.02	0.003	
0.01	58.97	20.89	15.17	4.51	0.100	
0.05	59.02	17.68	16.49	6.03	0.130	



Figure 2. FTIR spectra of the resulting membranes prepared under various Fe<sup>3+</sup> concentration in the coagulation bath

group. The C-O function of the carboxylic ester group was identified from the presence of peaks at 1297, 1239, 1148, 1104, and 1071 cm<sup>-1</sup>. In the double bond region (1300–2000 cm<sup>-1</sup>), peaks at 1406 and 1320 cm<sup>-1</sup> were related to sulfone groups (S=O stretching), while 1485 and 1577 cm<sup>-1</sup> represented stretching of C=C in cyclic alkanes.

Based on Figure 2, it can be observed that the modification of PES/DBR membrane with  $Fe^{3+}$  cocomponent has little influence on the transmission spectra. Some functional groups that show differences included C-H, S=O, and C=C. In membranes with  $Fe^{3+}$  concentrations of 0.01 and 0.05 M, lower transition was observed (where the peak was sharper). Conversely, at concentrations of 0.001 and 0.05 M, higher transition was observed. The reduction in transition is equivalent to an increase in adsorption, indicating an increase in these groups.

The principal component analysis (PCA) can be used to analysed data where the observations are described by a number of correlated quantitative dependent variables and was implemented to the FTIR spectra data. PCA represents statistical data as a set of new orthogonal variables called principal components. The goal is to extract important information from the data and present it in the form of clusters. The principal components in Figure 3 show that all variables were on the same PC 1 axis, suggesting there is no difference in peak wavelength or new peak in this finding.



Figure 3. Principal component analysis of the FTIR spectra

Different trend was observed on the PC 2 axis, where membranes with  $Fe^{3+}$  concentrations of 0.001 and 0.005 M were negatively correlated with M-3 (PES/DBR 0 M), while membranes with  $Fe^{3+}$  concentrations of 0.01 and 0.05 M were positively correlated.

In this finding, positive correlation indicated an increase in absorption percentage, vice versa. Both qualitatively and quantitatively, the results showed membranes with higher  $Fe^{3+}$ concentrations (0.01 and 0.05 M) had more hydrophobic groups, namely C-H, S=O, and C=C. This finding supported the findings on the water contact angle in which the membrane had higher values. FTIR analysis is generally used to identify functional groups present in organic compounds, explaining the absence of  $Fe^{3+}$ from identification.

# Cross-sectional morphology and analyses elementals

The structures of all membranes are shown in Figure 4. The cross-sectional morphology was obtained using SEM at  $3k \times and 10k \times$ . Overall, the morphology of the membrane was asymmetric shape, typically obtained from the phase inversion fabrication method. The structure consisted of a dense layer on the active side for foulant separation, and a support layer in the highly porous structure. The support layer has a cavity-like shape. The similarity of all samples was attributed to the same composition in each dope solution of 14.5% PES and 3% DBR.

Based on a qualitative analysis of SEM images at a  $3k\times$ , the concentration of  $Fe^{3+}$  did not significantly affect the thickness of the membrane except at a of 0.001 M. Similarly, the thickness of the support layer of the membrane did not show any significant changes. However, a clear trend can be seen from the  $10k\times$ , where changes could be seen in the width of the finger like cavities. Increasing the concentration of  $Fe^{3+}$  from 0.001 to 0.01 M widened the finger like cavities.

The interaction between hydroxyl groups in the dope solution and  $Fe^{3+}$  in the coagulation bath during the phase inversion could affect on the properties of the resulting membrane. The formation of the coordination complex could affect the precipitation and morphology of the resulting membrane by altering the rate of solvent diffusion and the polymer-nonsolvent interactions. The complex might reduce the diffusivity of the polymer in the coagulation bath, lowering the demixing rate resulting in a denser and compact structure. The presence of Fe atoms on the membrane has been confirmed at concentrations of 0.01 and 0.05 M, as indicated in Table 2. The highest percentage of these atoms is observed on the membrane surface.

### Porosity and mean pore radius

The analysis of the results presented in Table 3 reveals that alterations in the concentration of Fe<sup>3+</sup> have a discernible impact on both the porosity and pore size of the PES/DBR membranes. Specifically, elevating the Fe<sup>3+</sup> concentration to 0.005 M led to the creation of a more porous membrane, whereas a tenfold increase in concentration reduced the porosity. This observed trend was in line with the trend in both the water contact angle and water uptake. Furthermore, the average pore diameter, determined using the Guerout-Elford-Ferry equation, displayed a marked dependence on porosity and pure water flux, resulting in generally linear trends, as shown in Table 3. Within these findings, it was evident that as the Fe<sup>3+</sup> concentration raised, the average pore diameter decreased, with the exception of the concentration of 0.001 M. On the whole, the prepared membrane fell within the ultrafiltration category, characterized by pore sizes of less than 0.1 µm.

In the broader context, membrane porosity assumes a pivotal role in determining permeation performance, while pore size significantly influences the selective retention of substances. The primary objective of modifying hydrophobic membranes, aside from enhancing their resistance to fouling, is to enhance their permeability and selectivity. Alterations to membrane pore characteristics are typically introduced during the phase separation process of polymer solutions in membrane formation. These modifications can be achieved through various methods, such as adjusting the affinity between the solvent and non-solvent, reducing polymer concentration, incorporating hydrophilic additives, and raising the temperature, all of which contribute to an increase in surface porosity and pore size.

Within the scope of this study, the introduction of  $Fe^{3+}$  into the coagulation bath exerted a discernible impact on the thermodynamics during the solidification process. Specifically, concentrations of up to 0.001 M led to the formation of larger pores, while higher concentrations resulted in the formation of smaller pores.



Figure 4. The effect of Fe<sup>3+</sup> concentration on cross-sectional morphology.

Conc. of Fe <sup>3+</sup> in coagulation bath (M)	Porosity (%)	Average pore diameter (µm)
0	52.26	0.07482
0.001	54.48	0.07536
0.005	62.04	0.07217
0.01	52.66	0.06932
0.05	50.05	0.06821

# Effect of Fe<sup>3+</sup> concentration on the filtration performance

#### Pure water permeability

Figure 5 shows the influence of Fe<sup>3+</sup> concentration in the coagulation bath on the pure water permeability of the membrane. The pure water permeabilities were 143.28±0.33, 154.98±1.59, 160.80±2.24, 124.36±5.41, and 111.87±2.38 L/m<sup>2</sup>.h.bar at Fe<sup>3+</sup> concentrations of 0, 0.001, 0.005, 0.01, and 0.05 M, respectively. The change in pure water permeability observed in membranes with Fe<sup>3+</sup> concentrations of 0.001 and 0.05 M can be attributed to a higher water uptake, specifically 74.65% and 75.59%, which subsequently increased water absorption. Furthermore, the role of membrane porosity is underscored in increasing permeate flux by 54.48% (0.001 M) and 62.04% (0.05 M), as opposed to 52.26% in the absence of  $Fe^{3+}$ .

The concentration of  $Fe^{3+}$  within the coagulation bath was found to significantly influence the water permeability of the membrane. In general, higher concentrations of  $Fe^{3+}$  were associated with greater water permeability in the resulting membrane. During the coagulation process,  $Fe^{3+}$  ions interacted with the polymer molecules within the precursor solution, facilitating crosslinking and aggregation, ultimately resulting in a solid membrane structure. Higher concentrations of  $Fe^{3+}$  ions led to enhanced crosslinking and aggregation, yielding a more open, porous structure characterized by larger pores and increased water permeability. Conversely, excessive Fe<sup>3+</sup> concentrations could result in the formation of a dense, impermeable membrane structure, with a low water permeability.

In this study, an increase in Fe<sup>3+</sup> concentration, specifically at 0.01 and 0.05 M, led to a decrease in pure water permeability. This reduction was attributed to changes in the physicochemical characteristics of the membrane, particularly a reduced water uptake of 73.43% and 72.70%. The decrease in flux of up to 13.20% (0.01 M) and 21.92% (0.05 M) was also influenced by the decrease in membrane porosity to 52.66% and 50.05%, along with the narrowing of fingerlike channels. Thus far, the optimal characteristics and permeability were observed in the PES/DBR membrane with an Fe<sup>3+</sup> concentration of 0.005 M. Previous studies have also documented this phenomenon, where membrane permeability decreases at higher Fe concentrations.

#### Humic acid permeability and selectivity

Figure 6 illustrates the influence of  $Fe^{3+}$  concentration on both the permeability and rejection of humic acid solution. The permeability of humic acid was examined for M1–M5 yielding values of 125.72±2.22, 125.68±4.84, 134.50±0.15, 114.04±3.23, and 106.82±2.77, respectively. Notably, the observed trend in humic acid permeability closely mirrors the pattern observed in the permeability of pure water, as depicted in Figure 6, with a consistent percentage decrease of approximately 12%. The variation in humic acid



Figure 5. The effect of Fe<sup>3+</sup> concentration in the coagulation bath on the pure water permeability of the membranes



Figure 6. The effect of Fe<sup>3+</sup> concentration on humic acid solution permeability and selectivity

solution permeabilities can be attributed to the inherent characteristics of the membranes, specifically their water uptakes and porosities.

The rejections of humic acid were 97.41%, 97.68%, 97.91%, 98.54%, and 99.17% at varying Fe<sup>3+</sup> concentrations from M1 to M5, respectively. An increase in Fe<sup>3+</sup> concentration was associated with the change of humic acid rejection, primarily owing to a reduction in pore size. The selectivity of the membrane was notably influenced by pore size, with the average pore diameter ranging from 0.065 to 0.075 µm in all the prepared membranes. It's worth noting that a minor slight decrease in rejection  $(\pm 1.06\%)$  was observed in the PES/DBR membrane with lower Fe<sup>3+</sup> concentrations. Consequently, membranes featuring Fe<sup>3+</sup> concentrations of 0.001 and 0.005 M continued to demonstrate superior performance in terms of both permeability and selectivity.

#### Antifouling

Fouling's impact on the membrane is evident in the reduced permeability observed during the filtration process. In this study, the membrane's anti-fouling capacity was assessed by computing the FRR. The FRR quantifies the percentage of the membrane's capability to reinstate its ability to pass pure water after fouling. This evaluation entailed a specific sequence of steps: the membrane underwent compaction for 60 minutes by the passage of distilled water. Subsequently, over the following 60 minutes, the weight of the filtrate was measured to determine the initial pure water flux  $(J_{w1})$ . Filtration continued with a 50-ppm humic acid solution for 60 minutes  $(J_{ha})$ , during which the flux decreased. A backwash procedure using distilled water was then applied for 10 minutes, followed by pure water filtration after washing for 120 minutes  $(J_{w2})$ . The outcomes of these procedures were used to calculate the FRR, as depicted in Figure 7.

As indicated by Figure 7, it is evident that the variation in Fe<sup>3+</sup> concentration applied to the PES/DBR membrane correlated well with a reduction in the FRR. The flux recovery exhibited a diminishing trend as the concentration increased, with values of 94.77±0.50, 94.76±0.76, 92.24±1.70, 93.44±1.95, and 91.65±0.80%, respectively. The anti-fouling efficacy of the membrane is closely associated with its hydrophilicity, specifically the contact angle exhibited on its surface. A hydrophilic surface readily induces the formation of a hydration layer at the interface between the membrane and water. This layer plays a critical role in repelling foulant, such as humic acid, characterized by its hydrophobic properties. The PES/DBR membrane featuring a Fe<sup>3+</sup> concentration of 0 M displays the lowest water contact angle of 58.66°, resulting in the highest FRR of 94.77%. In general, the membranes exhibited satisfactory FRR, surpassing the 90% mark. Although there is a slight reduction observed, but insignificant. These findings align with the attributes associated with the water contact angle of the membrane summarized in Table 1.



Figure 7. The effect of Fe<sup>3+</sup> concentration on flux recovery

#### Membrane chemical stability

Based on our earlier report (Ambarita, Mulyati, Arahman, Bilad, et al., 2024), it has been established that DBR exhibited a diminished stability when exposed to highly alkaline conditions. This instability raised from the leaching of DBR, attributed to its strong affinity for water. Previous work suggested that enhancing the chemical bond stability of the additive within the polymer's primary structure could be achieved by incorporating co-components featuring covalent bonds. As a result, the assessment of chemical stability assumes paramount importance and was evaluated in this study. The evaluation process commenced with the measurement of the permeability of pure water and humic acid solution for each membrane on day 0, enabling the collection of initial flux  $(J_{w1})$  and rejection  $(R_1)$  data. Subsequently, the membranes were immersed in a highly alkaline solution, specifically 0.01 N NaOH (pH: 12), for a duration of 48 hours, using a volume of 50 mL. Post-immersion, the membranes underwent rinsing with distilled water to eliminate any remaining NaOH solution. Following this, permeability measurements for both pure water and humic acid solution were conducted to acquire the final flux  $(J_{w2})$ and rejection  $(R_{a})$  data. The assessment of chemical stability was based on the ratio of changes in flux and rejection, as depicted in Figures 8 and 9.

As depicted in Figure 8, an increase in Fe<sup>3+</sup> concentration corresponded to a reduction in the pure water flux ratio. The increment ratios in flux associated with rising Fe<sup>3+</sup> concentrations were

1.406, 1.376, 1.380, 1.316, and 1.251, respectively. This modification, however, was not effective in preventing the leaching of the PES/DBR membrane. The average percentage increase in flux across various Fe<sup>3+</sup> concentrations was 33.08%, and this increase was statistically significant statistically (p-value > 0.1). Notably, the membrane featuring a Fe<sup>3+</sup> concentration of 0.005 M demonstrated the lowest flux increase ratio. This specific membrane succeeded in reducing the increase in pure water permeability within the membrane without co-component combinations by 15.50%. In accordance with prior research, the M-3 (PES with the addition of 3% DBR) experienced alterations in performance when exposed to a strong base (0.1 N NaOH for 5 days), resulting in a 90.74% increase in pure water permeability likely due to pore enlargement due to pore size swelling.

In contrast to permeability, an escalation in Fe<sup>3+</sup> concentration correlated with an increase in the humic acid rejection ratio (Fig. 9). The computed data yielded ratios of 0.918, 0.969, 0.963, 0.967, and 0.981, respectively. The average percentage decrease in rejection across various Fe<sup>3+</sup> concentrations was merely 3%, and this decrease was not considered statistically significant. Ordinarily, as flux increases, rejection tends to decrease due to the enlargement of membrane pore size. However, intriguingly, this study observed that despite the relatively high percentage increase in water flux, standing at 33.08%, the membrane's rejection rate remained commendable (i.e., greater than 90%). The membrane featuring



Figure 8. The effect of Fe<sup>3+</sup> concentration on ratio of water permeability



Figure 9. The effect of Fe<sup>3+</sup> concentration on ratio of humic acid rejection

a Fe<sup>3+</sup> concentration of 0.005 M emerged as the best in sustaining rejection, with a marginal 1.9% decrease in rejection after immersion in 0.01 N NaOH for 48 hours.

It is noteworthy that *Daemonorops spp.* species' DBR for coloration is primarily composed of dracorhodin and dracorubin compounds (Waluyo & Wibowo, 2018). These compounds encompass various polyphenolic elements, including flavonoids and anthocyanins, which impart the red coloration. Both groups exhibit polarity, allowing them to dissolve in water. As established in prior studies, the orange color results from the release of a small quantity of hydrophilic red colorants. The leaching of DBR is attributed to the degradation of hydrophilic components induced by hydroxide ions, especially in high alkaline conditions. It was suggested that formation of coordinate covalent bonds between anthocyanin (as a colorant component) and  $Fe^{3+}$  enhanced the performance stability, as illustrated in Figure 10.

Figure 10 provides a conceptual representation of the interaction between the hydroxyl group in DBR and  $Fe^{3+}$ . It is feasible that this



Figure 10. The coordination interaction mechanism between DBR and Fe<sup>3+</sup>

bond might not exhibit the same strength as the bond between the galloyl group (present in tannic acid) and  $Fe^{3+}$  due to the absence of a galloyl group in anthocyanin. This notion is supported by the findings presented in Figure 8, where this modification failed to prevent DBR leaching from the PES/DBR membrane. However, membranes featuring higher  $Fe^{3+}$  concentrations demonstrated the most modest flux enhancement ratios.

According to the literature, tannic acid contains polyphenolic compounds, where DBR also has (Perron & Brumaghim, 2009). The chemical structure of TA is usually given as decagalloyl glucose  $(C_{76}H_{52}O_{46})$ , which is actually a polygalloyl mixture of glucose molecules with different degrees of esterification. In TA, there are two hydroxyl groups (-OH) adjacent to the catechol group (Ejima et al., 2013; Yang et al., 2015). Meanwhile, in DBR, there are two adjacent hydroxyl groups (-OH) in the flavan ring system, making it possible to bind metal ion sites. Figure 10 illustrates the expected reaction between the hydroxyl group in DBR and Fe<sup>3+</sup>. It is possible that this bond is not as strong as the bond between the galloyl group (in tannic acid) and Fe<sup>3+</sup> because anthocyanin does not contain a galloyl group. It is supported by the results in Figure 8, where this modification could not prevent leaching on the PES/DBR membrane. However, membranes with high Fe<sup>3+</sup> concentrations offered the lowest flux enhancement ratios.

### CONCLUSIONS

In conclusion, the study found that increasing the Fe<sup>3+</sup> concentration in the PES/DBR membrane had significant effects on the resulting membranes' characteristics and performance. Specifically, higher Fe<sup>3+</sup> concentrations led to alterations in the cross-sectional structure of the membrane, resulting in narrower finger-like channels, reduced porosity, and lowered average pore size. As a consequence, at a  $Fe^{3+}$  concentration of 0.05 M, water permeability decreased by 21.68%. Despite this decrease in water permeability, the membrane demonstrated impressive humic acid rejection  $(R_{HA} > 97\%)$  and good antifouling properties (FRR > 91%). The formation of coordinate covalent bonds between DBR (anthocyanins as colorant content) and Fe<sup>3+</sup> aimed to enhance the membrane's chemical stability. It was proven by the ratio of permeation rates and humic acid rejection before and after immersion. This research suggests that a Fe<sup>3+</sup> concentration of 0.05 M is worthy of further investigation, particularly regarding its long-term performance in extreme acidic and alkaline conditions, offering valuable insights for our future studies.

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